PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-097222
(43)Date of publication of application : 09.04.1999

(51)Int.Cl. H01F 1/053
B22F 1/00
H01F 1/06
H01F 7/02
// C22C 38/00

(21)Application number : 09-255255
(22)Date of filing : 19.09.1997

(71)Applicant : SHIN ETSU CHEM CO LTD
(72)Inventor : NOMURA TADAO
OHASHI TAKESHI

(54) ANISOTROPIC RARE EARTH PERMANENT MAGNET MATERIAL AND MAGNET POWDER

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a composition wherein readily magnetizable axes of hard magnetic phases are oriented in a uniaxial direction, by deforming, with pressure, a quenched thin strip of alloy material in uniaxial direction while being heated.
SOLUTION: A hard magnetic phase of an anisotropic rare earth permanent magnet is composed of $Nd_2Fe_{14}B$, and a soft magnetic phase thereof contains at least one or more kinds from bcc-Fe, Fe_3B and Fe_2B, the percentage of which being 10-90% of the entire volume. The melt of this composition alloy is quenched to obtain a quenched thin strip of alloy in a form of amorphous, or a mingling of amorphous and christallites. The composition of this case is so made that the hard magnetic phase and the soft magnetic phase are finely dispersed and deposited by heat treatment. Subsequently, a sample from the resultant is subjected to grinding, followed by deformation, with pressure, at a high temperature, thereby obtaining the anisotropic rare earth permanent magnet having a

composition wherein readily magnetizable axes of the hard magnetic phases are oriented in uniaxial direction.

LEGAL STATUS

[Date of request for examination]	19.07.2000
[Date of sending the examiner's decision of rejection]	13.08.2003
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	
[Date of registration]	
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

CLAIMS

[Claim(s)]
[Claim 1] The anisotropy rare earth permanent magnet characterized by arranging the easy axis of a hard magnetism phase with an one direction by carrying out pressurization deformation at 1 shaft orientations in the rare earth permanent magnet which has the internal organization which the hard magnetism phase and the soft magnetism phase distributed minutely where the alloy raw material of a quenching thin band is heated.
[Claim 2] The anisotropy rare earth permanent magnet according to claim

1 whose hard magnetism phase is Nd2Fe14B and whose volume percentage of a soft magnetism phase the soft magnetism phase contains at least one or more sorts in bcc-Fe, Fe3B, and Fe2B, and is 10 - 90%.
[Claim 3] a hard magnetism phase -- Nd2(Fe, Co) 14B it is -- a soft magnetism phase -- Fe-Co An alloy, 3(Fe, Co) B, and 2B (Fe, Co) Anisotropy rare earth permanent magnet according to claim 1 whose volume percentage of a soft magnetism phase at least one or more sorts are included inside, and is 10 - 90%.
[Claim 4] a hard magnetism phase -- Sm2Co17 Sm2 (Fe, Co) 17 [or] -- it is -- a soft magnetism phase -- Co -- or -- Anisotropy rare earth permanent magnet according to claim 1 whose volume percentage of a soft magnetism phase the Fe-Co alloy is included and is 10 - 90%.
[Claim 5] A hard magnetism phase is Sm (Fe, M1)12. Or it is Sm (Fe, Co, M1)12. a soft magnetism phase -- bcc-Fe -- or -- A Fe-Co alloy and Fe-M1 an alloy -- Fe-M1 At least one or more sorts in an intermetallic compound, Fe-Co-M1 alloy, and Fe-Co-M1 intermetallic compound are included (however, M1). The anisotropy rare earth permanent magnet according to claim 1 one or more sorts in Ti, V, Cr, Mo, Si, and Cu and whose volume percentage of a soft magnetism phase are 10 - 90%.
[Claim 6] a hard magnetism phase -- Sm2Fe17 a nitride or Sm2 (Fe, Co) 17 nitride -- it is -- a soft magnetism phase -- bcc-Fe -- or -- Anisotropy rare earth permanent magnet according to claim 1 whose volume percentage of a soft magnetism phase the Fe-Co alloy is included and is 10 - 90%.
[Claim 7] A hard magnetism phase is a FeX (Nd, M2) nitride or (Nd, M2) (Fe, Co) X. It is a nitride (however, 5<=X<=12). A soft magnetism phase is bcc-Fe and Fe-M2. An alloy and Fe-M2 Intermetallic compound, Fe-Co At least one or more sorts in an alloy, Fe-Co-M2 alloy, and Fe-Co-M2 intermetallic compound are included (however, M2). The anisotropy rare earth permanent magnet according to claim 1 one or more sorts in Ti, V, Zr, Nb, Hf, Ta, Si, and aluminum and whose volume percentage of a soft magnetism phase are 10 - 90%.
[Claim 8] Anisotropy rare earth magnet powder obtained by grinding a magnet according to claim 1.
[Claim 9] Anisotropy rare earth permanent magnet powder according to claim 8 whose hard magnetism phase is Nd2Fe14B and whose volume percentage of a soft magnetism phase the soft magnetism phase contains at least one or more sorts in bcc-Fe, Fe3B, and Fe2B, and is 10 - 90%.
[Claim 10] a hard magnetism phase -- Nd2(Fe, Co) 14B it is -- a soft magnetism phase -- Fe-Co An alloy, 3(Fe, Co) B, and 2B (Fe, Co) Anisotropy rare earth permanent magnet powder according to claim 8 whose volume percentage of a soft magnetism phase at least one or more sorts

are included inside, and is 10 - 90%.
[Claim 11] a hard magnetism phase -- Sm2Co17 Sm2 (Fe, Co) 17 [or] -- it is -- a soft magnetism phase -- Co -- or -- Anisotropy rare earth permanent magnet powder according to claim 8 whose volume percentage of a soft magnetism phase the Fe-Co alloy is included and is 10 - 90%.
[Claim 12] A hard magnetism phase is Sm (Fe, M1)12. Or it is Sm (Fe, Co, M1)12. a soft magnetism phase -- bcc-Fe -- or -- A Fe-Co alloy and Fe-M1 an alloy -- Fe-M1 At least one or more sorts in an intermetallic compound, Fe-Co-M1 alloy, and Fe-Co-M1 intermetallic compound are included (however, M1). Anisotropy rare earth permanent magnet powder according to claim 8 one or more sorts in Ti, V, Cr, Mo, Si, and Cu and whose volume percentage of a soft magnetism phase are 10 - 90%.
[Claim 13] a hard magnetism phase -- Sm2Fe17 a nitride or Sm2 (Fe, Co) 17 nitride -- it is -- a soft magnetism phase -- bcc-Fe -- or -- Anisotropy rare earth permanent magnet powder according to claim 8 whose volume percentage of a soft magnetism phase the Fe-Co alloy is included and is 10 - 90%.
[Claim 14] A hard magnetism phase is a FeX (Nd, M2) nitride or (Nd, M2) (Fe, Co) X. It is a nitride (however, 5<=X<=12). A soft magnetism phase is bcc-Fe and Fe-M2. An alloy and Fe-M2 Intermetallic compound, Fe-Co At least one or more sorts in an alloy, Fe-Co-M2 alloy, and Fe-Co-M2 intermetallic compound are included (however, M2). Anisotropy rare earth permanent magnet powder according to claim 8 one or more sorts in Ti, V, Zr, Nb, Hf, Ta, Si, and aluminum and whose volume percentage of a soft magnetism phase are 10 - 90%.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to an anisotropy rare earth permanent magnet and magnet powder.
[0002]
[Description of the Prior Art] current and rare earth permanent magnet A Sm-Co system and Nd-Fe-B although the system etc. is fertilized -- especially -- magnetic properties with an expensive Nd-Fe-B magnet -- having -- moreover, Sm-Co Since ingredient cost is low as compared with a system magnet, need is growing. This Nd-Fe-B Some processes are developed by the permanent magnet. But the manufacture approach that industrialization is progressing is a sintering process. Although it has the organization which this sintered magnet made the main phase Nd2Fe14B which has hard magnetic property, and contained Nd rich phase and the Nd1.1Fe4 B4 phase (B rich phase) further After grinding the alloy which dissolved by the presentation with Nd and B to several micrometers fines and arranging an easy axis with an one direction with shaping among a magnetic field rather than Nd2Fe14B stoichiometric composition as a process, [superfluous a little] Sinter at the temperature near 1100 degree C, and the approach of carrying out low-temperature aging treatment further (M. Sagawa et al and Japanese Journal of Applied Physics 26 (1987) 785) is learned. Coercive force is discovered in an interface being cleaned with Nd rich phase in which the Nd2Fe14B main phase enclosed the perimeter, and it becomes an anisotropy permanent magnet. On the other hand, the approach of producing a quenching thin band alloy and producing a magnet based on this by the melt span method for blowing off and carrying out high-speed coagulation of the molten metal of a magnet presentation on a roll kneader, is also developed (R. W.Lee, Physics Letter 46 (1985) 790, etc.). Although this magnet similarly makes Nd2Fe14B the main phase, the diameter of crystal grain is small compared with 20 to 100 nm, and a sintered magnet, and it has become the reason of coercive force that it is single domain particle size. There are three types of these. Although this is easy a process, it is not equal to an one direction, and since pack density is low, magnetic properties are inferior [it mixes / resin and /, and the 1st type fabricates what ground the quenching thin band and is used as a bond magnet, and / it is isotropy, and] in an easy axis. The 2nd type carries out the hotpress of this quenching thin ****, and is used as an isotropic bulk magnet, and the 3rd type performs hot working to this further, and arranges an easy axis in the pressurization direction (JP,60-100402,A etc.).

[0003] On the other hand, while next-generation magnet retrieval of the further high performance is performed, the nano composite magnet attracts attention in recent years (E. F.Kneller et al and IEEE Transaction Magnetics 27 (1991) 3588 others). Fe(s), such as bcc-Fe and Fe3B of what makes the main phase the Nd2Fe14 B phase the above-mentioned sintered magnet and whose quenching magnet are hard magnetism phases, and Fe2B, -- the rich soft magnetism phase is not included. On the other hand, a nano composite magnet consists of an organization where the hard magnetism phase and the soft magnetism phase carried out detailed distribution to dozens of nm order, and by the exchange interaction, by Lycium chinense with an epilogue, magnetization of a bi-phase is not easily reversed and serves magnetization of a soft magnetism phase like a hard magnetism phase single as a whole. Higher saturation magnetization may be obtained also in the combination of the existing ingredient, without spoiling coercive force by this. It anisotropy-ized in count. Sm2Fe17N3/Fe-Co It sets and the value of (BH) max =137 MGOe is reported (R. Skomski et al, Physical Review B 48 (1993) 15812). As an example of an experiment which actually produced the nano composite magnet Former Nd2Fe14B/Fe3B (R. Coehoorn et al and Journal de Physique 49(1988) C 8-669), Nd2Fe14 B/Fe (JP,7-173501,A and JP,7-176417,A --) L. Withanawasam et al and Journal of Applied Physics 76 (1994) 7065 etc. Combination, such as Sm2Fe17N3/Fe (J. Ding et al, Journal of Magnetism and Magnetic Materials 124 (1993)L1), is reported. however, the quenching thin band according each to the melt span method as the production approach of a detailed distribution organization currently performed by these researches and mechanical alloying (MA) -- since means to heat-treat and microcrystal-ize the end of an amorphous alloy powder it was obtained by law are taken, the way things stand, crystal orientation cannot arrange as well as the 1st above-mentioned type, but only an isotropic thing is obtained magnetically. Therefore, there is no report which produced the anisotropy nano composite magnet to this time, and it waits for the implementation.

[0004]

[Problem(s) to be Solved by the Invention] Thus, although the nano composite permanent magnet which has a magnetic anisotropy is reported by count and the theory, there is no report actually produced until now. This invention makes it a technical problem to realize an anisotropy rare earth permanent magnet with the organization to which the hard magnetism phase and the soft magnetism phase distributed minutely, and the easy axis of a hard magnetism phase is equal by adding the further amelioration to the conventional production approach.

[0005]
[Means for Solving the Problem] In order to solve this problem, as a result of inquiring wholeheartedly, by carrying out hot working of the quenching thin band alloy of a presentation in which a hard magnetism phase and a soft magnetism phase carry out a detailed distribution deposit by heat treatment, this invention persons established a header and terms and conditions for the above-mentioned rare earth permanent magnet being obtained, and completed this invention. That summary has the easy axis of a hard magnetism phase in the anisotropy rare earth magnet powder obtained by the anisotropy rare earth permanent magnet arranged with the one direction, and this grinding in the rare earth permanent magnet which has the internal organization which the hard magnetism phase and the soft magnetism phase distributed minutely by carrying out pressurization deformation at 1 shaft orientations, where the alloy raw material of a quenching thin band is heated.
[0006]
[Embodiment of the Invention] The hard magnetism phase of the above-mentioned anisotropy rare earth permanent magnet Nd2Fe14B and Nd2(Fe, Co) 14B, Sm2Co17, Sm2 (Fe, Co) 17, and Sm (Fe, M1)12, Sm (Fe, Co, M1)12 (M1 [however,] -- Ti, V, Cr, and Mo --) One or more sorts in Si and Cu, and Sm2Fe17 A nitride, Sm2 (Fe, Co) 17 nitride, (Nd, M2) a FeX nitride or (Nd, M2) (Fe, Co) X nitride (5<=X<=12 and M2 -- Ti --) [however,] It is the phase chosen from one or more etc. sorts in V, Zr, Nb, Hf, Ta, Si, and aluminum etc. A soft magnetism phase is bcc-Fe, Fe3B, Fe2B, and Fe-Co. Alloy, (Fe, Co) 3B, 2B (Fe, Co), and Fe-M1 Alloy, Fe-M1 An intermetallic compound, Fe-Co-M1 alloy, Fe-Co-M1 intermetallic compound, Fe-M2 An alloy and Fe-M2 At least one or more sorts, such as an intermetallic compound, Fe-Co-M2 alloy, and Fe-Co-M2 intermetallic compound, are included, and the volume percentage of a soft magnetism phase is 10 - 90%.
[0007] The hard magnetism phase of the above-mentioned magnet powder Moreover, Nd2Fe14B and Nd2(Fe, Co) 14B, Sm2Co17, Sm2 (Fe, Co) 17, and Sm (Fe, M1)12, Sm (Fe, Co, M1)12 (M1 [however,] -- Ti, V, Cr, and Mo --) One or more sorts in Si and Cu, and Sm2Fe17 A nitride, Sm2 (Fe, Co) 17 nitride, (Nd, M2) a FeX nitride or (Nd, M2) (Fe, Co) X nitride (5<=X<=12 and M2 -- Ti --) [however,] It is the phase chosen from one or more etc. sorts in V, Zr, Nb, Hf, Ta, Si, and aluminum etc. A soft magnetism phase is bcc-Fe, Fe3B, Fe2B, and Fe-Co. Alloy, (Fe, Co) 3B, 2B (Fe, Co), and Fe-M1 Alloy, Fe-M1 An intermetallic compound, Fe-Co-M1 alloy, Fe-Co-M1 intermetallic compound, Fe-M2 An alloy and Fe-M2 At least one or more sorts, such as an intermetallic compound, Fe-Co-M2 alloy, and Fe-Co-M2

intermetallic compound, are included, and the volume percentage of a soft magnetism phase is 10 - 90%.

[0008] Below, this invention is explained to a detailed explanation. The final organization consists of the condition that the hard magnetism phase and the soft magnetism phase distributed minutely, and the easy axis of a hard magnetism phase was arranged with the one direction, in this invention. A hard magnetism phase Nd2Fe14B, Nd2(Fe, Co) 14B, and Sm2Co17, Sm2 (Fe, Co) 17, Sm (Fe, M1)12, and Sm (Fe, Co, M1)12 (M1 [however,] -- Ti --) One or more sorts in V, Cr, Mo, Si, and Cu, following **, and Sm2Fe17 Nitride, Sm2 (Fe, Co) 17 nitride, a FeX (Nd, M2) nitride, or (Nd, M2) (Fe, Co) X nitride (5<=X<=12 and M2 -- Ti --) [however,] It is the phase chosen from one or more sorts in V, Zr, Nb, Hf, Ta, Si, and aluminum, following **, etc. A soft magnetism phase is bcc-Fe, Fe3B, Fe2B, and Fe-Co. Alloy, (Fe, Co) 3B, 2B (Fe, Co), and Fe-M1 Alloy, Fe-M1 An intermetallic compound, Fe-Co-M1 alloy, Fe-Co-M1 intermetallic compound, Fe-M2 An alloy and Fe-M2 At least one or more sorts, such as an intermetallic compound, Fe-Co-M2 alloy, and Fe-Co-M2 intermetallic compound, are included, and the volume percentage of a soft magnetism phase is 10 - 90%.

[0009] Production of this magnet is performed as follows. The quenching thin band alloy with which the melting object of a predetermined presentation alloy was first quenched, and the microcrystal was intermingled as it is amorphous or amorphous is produced. The presentation at this time is considered as a presentation in which a hard magnetism phase and a soft magnetism phase carry out a detailed distribution deposit by heat-treating. Moreover, it is made for the volume rate of the soft magnetism phase in a final sample to become 10 - 90%. At less than 10%, improvement in saturation magnetization is slight and there is no merit used as a nano composite magnet. Moreover, when it exceeds 90%, there are too few hard magnetism phase rates, and a magnetic coercive force fall is remarkable.

[0010] When a concrete ingredient is described, for example the combination of a hard magnetism phase / soft magnetism phase is Nd2Fe14 B/bcc-Fe hereafter When it is desirable to consider as the presentation of an about [Fe-2-10at% Nd-1-8at%B] and it is Nd2Fe14B/Fe3B The presentation of an about [Fe-2-10at% Nd-15-25at%B] is desirable. Moreover, in the case of Nd2Fe14 B/Fe2B, it is. The presentation of an about [Fe-2-10at% Nd-25-35at%B] is desirable. Moreover, by choosing these middle presentations, it can also be made the organization in which soft magnetism phases, such as bcc-Fe, Fe3B, and Fe2B, live together.

[0011] permuting a part of Fe by Co -- Nd2 (Fe, Co)14B/Fe-Co An alloy, Nd2 (Fe, Co)14B / (Fe, Co) 3B, and Nd2 (Fe, Co)14B / (Fe, Co) 2B etc. -- it is good also as a combination. In order to raise a property furthermore, some kinds of elements chosen from aluminum, Si, Ti, V, Cr, Mn, nickel, Cu, Zn, Ga, germanium, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl, Pb, Bi, etc. may be added in the form where Fe is permuted. If there are too many additions at this time, in order to cause the fall of saturation magnetization, as for the amount of permutations, many and less than [5at%] are desirable. Moreover, in order to raise coercive force further, a part of Nd may be permuted by other rare earth elements, such as Pr, Tb, Dy, and Ho.
[0012] The presentation of Co-2-10at%Sm extent is desirable the time of a hard magnetism phase / soft magnetism phase being Sm2Co17 / Co. Moreover, a part of Co may be permuted by Fe, and it may consider as an Sm2(Fe, Co) 17-/Fe-Co alloy, or you may permute by the above-mentioned element group for the improvement in a property, and a part of Sm may be further permuted by other rare earth elements and misch metals, such as Ce.
[0013] A hard magnetism phase / soft magnetism phase Although M1 element is required in order to stabilize the one to 12 above-mentioned crystal structure when it is Sm(Fe, M1) 12/bcc-Fe, the optimal presentation changes with elements. for example, SmFe11Ti is stable at the time of M1=Ti -- carrying out -- the times, such as V, Cr, Mo, and Si, -- SmFe10M12 Since it is easy to stabilize, a start presentation is adjusted according to an element. Moreover, a soft magnetism phase is Fe-M1 in addition to bcc-Fe. An alloy and Fe-M1 You may be an intermetallic compound. Furthermore, a part of Fe is permuted by Co, and it is Sm (Fe, Co, M1)12/Fe-Co. An alloy, Consider as Sm (Fe, Co, M1)12/Fe-Co-M1 alloy and Sm (Fe, Co, M1)12/Fe-Co-M1 intermetallic compound, or In order to raise a property furthermore aluminum, Mn, nickel, Cu, Zn, Ga, Some kinds of elements chosen from germanium, Zr, Nb, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Hf, Ta, W, Re, Os, Ir, Pt, Au, Tl, Pb, Bi, etc. may be added in the form where Fe is permuted. Furthermore, a part of Sm may be permuted by other rare earth elements.
[0014] The presentation of Fe-2-10at%Sm extent is desirable the time of a hard magnetism phase / soft magnetism phase being Sm2 Fe17 nitride / bcc-Fe. Nitriding of a hard magnetism phase is performed to coincidence at the time of heat treatment of a back process. Also in this case, a part of Fe is permuted by Co, and they are Sm2 (Fe, Co) 17 nitride / Fe-Co. It may consider as an alloy, or you may permute by the above-mentioned element group, and a part of Sm may be permuted by other rare

earth elements.
[0015] A hard magnetism phase is a FeX (Nd, M2) nitride or (Nd, M2) (Fe, Co) X. When it is a nitride, About the FeX compound used as the radical of this nitride phase (Nd, M2), NdFe2, Nd2Fe17 etc. -- although it has the same crystal structure as a system stability phase of 2 yuan -- others and 1-7 Although many compounds, such as a compound, a metastable phase, etc. which are stabilized by plural systems like a phase and one to 12 phase, exist, therefore there is also many of the nitride When X is smaller than 5, a compound cannot serve as ferromagnetism easily due to a room temperature, and when X is larger than 12, it is hard to have sufficient magnetic anisotropy. Therefore, X of the FeX nitride which is a hard magnetism phase (Nd, M2) has the desirable range of 5<=X<=12. Moreover, a soft magnetism phase is not limited to bcc-Fe, either, but it is Fe-M2. An alloy and Fe-M2 An intermetallic compound or these may live together. It is what performs nitriding of a hard magnetism phase to coincidence also in this case at the time of heat treatment of a back process. Furthermore, a part of Fe is permuted by Co, and it is X (Fe (Nd, M2), Co). A nitride/Fe-Co An alloy and X (Fe (Nd, M2), Co) A nitride / Fe-Co-M2 alloy, (Nd, M2) X (Fe, Co) It may consider as a nitride / Fe-Co-M2 intermetallic compound etc., and you may permute by the above-mentioned element group, and a part of Nd may be permuted by other rare earth elements. If some concrete examples are given, Fe(Nd, Zr)7 nitride / bcc-Fe, Fe7 nitride / Fe-Zr, and Fe(Nd, Zr)7 nitride / Fe3Zr, (Nd, Zr) (Nd, Zr) 7 (Fe, Co) A nitride/Fe-Co, Fe(Nd, Zr)9 nitride / bcc-Fe, (Nd, Zr) 9 (Fe, Co) A nitride/Fe-Co, and Fe(Nd, Zr) 10 A nitride/bcc-Fe, (Nd, Zr) 10 nitrides / Fe-Co, and Fe(Nd, Zr) 12 (Fe, Co) A nitride/bcc-Fe, 12 nitrides / Fe-Co, Fe(Nd, Nb)7 nitride / bcc-Fe, (Nd, Zr) (Fe, Co) (Nd, Nb) 7 (Fe, Co) A nitride/Fe-Co, and Fe(Nd, Nb) 12 A nitride/bcc-Fe, 12 nitrides / Fe-Co, Fe(Nd, Hf)7 nitride / bcc-Fe, (Nd, Nb) (Fe, Co) (Nd, Hf) 7 (Fe, Co) A nitride/Fe-Co, and Fe(Nd, Hf) 12 A nitride/bcc-Fe, and 12 (Fe (Nd, Hf), Co) nitrides / Fe-Co etc. -- although it is, it is not limited to these.
[0016] as the quenching approach -- a roll kneader method and Sprat -- although law, the gas atomizing method, etc. are learned, the thing with the simple and quenching thin band by the roll kneader method which has good quality is obtained especially. In the roll made from Cu, it is 10 m/s. It is 50 m/s above. A good property is acquired at the following roll rates. 10 m/s A sample amorphous in the following cannot be obtained but it is 50 m/s. If it exceeds, crystallization by the next heat treatment process will become difficult. Next, after grinding this sample, pressurization deformation is carried out at an elevated

temperature. The approach (refer to JP,60-100402,A) of performing hot form, an extrusion method (Kojima et al. and the Magnetics Society of Japan 12 and 219 (1988)), a pack rolling method (Sakamoto et al. and the Magnetics Society of Japan 16 and 147 (1992)), the approach (refer to JP,7-87156,B) using impact pressure, etc. are used after solidification shaping by the hotpress as the approach of pressurization deformation. these -- each -- the former although used as the production approach of a Nd-Fe-B system anisotropic magnet -- $Nd_2Fe_{14}B$ stoichiometric composition -- Nd -- being tried about the rich presentation -- receiving -- this invention -- each -- the presentation with less rare earth than the stoichiometric composition of a hard magnetism phase -- it is -- bcc-Fe and Fe-Co The soft magnetism phase of an alloy and others is included 10 to 90%, and it is aimed at a presentation which is carrying out switched connection to the hard magnetism phase magnetically. Thus, the obtained bulk sample serves as an anisotropy rare earth permanent magnet which consists of an organization with which the hard magnetism phase and the soft magnetism phase distributed minutely, and the easy axis of a hard magnetism phase was equal to the one direction. By furthermore grinding this bulk magnet, the nano composite rare earth magnet powder which has an anisotropy is obtained. If mixed shaping of this is carried out with resin, the bond magnet of a high property is producible.

[0017]

[Example] Next, although an example is given and this invention is explained concretely, this invention is not limited to these.

(Examples 1-16) After carrying out weighing capacity so that it may become the predetermined presentation which shows each pure metal in Table 1, the alloy was obtained by the arc dissolution. This is put in in a quartz nozzle, the RF dissolution is carried out in Ar ambient atmosphere, and it is 45 m/s. It injected on the roll made from Cu which is rotating with peripheral velocity, and the quenching thin band was produced. Hot working of what ground this quenching thin band and was used as powder was carried out by following either. In addition, the approach of ** went, when using a hard magnetism phase as a nitride.

** It is hot form in Ar ambient atmosphere again after solidification with the hotpress in Ar ambient atmosphere.

** Press compression after filling up the container made from Cu and heating in Ar ambient atmosphere.

** Fill up the container made from Cu and it is N_2. It heats in an ambient atmosphere and is the press compression after forming a nitride.

The number of the approach chosen as Table 1 and the heat treatment

temperature at that time are written together. internal organization of the sample after production TEM -- or -- It observed by the SEM reflection electron image, and while checking existence of the soft magnetism phase which corresponds in an each sample, the rate of a volume ratio was judged. The ratios Ia1/Ip1 of the magnitude Ip1 of magnetization of the compression direction when carrying out 20kOe magnetic field impression and the magnitude Ia1 of magnetization in a direction perpendicular to compression performed the judgment of a magnetic anisotropy in the sample started in the cube form. It expresses that a magnetic anisotropy is so large that the value of Ia1/Ip1 is small. Moreover, the powder which carried out the ball milling of this bulk sample was hardened from paraffin all over 14kOe magnetic field, and parallel and the ratios Ia2/Ip2 of the magnitude Ip2 and Ia2 of the magnetization when carrying out 20kOe magnetic field impression were perpendicularly measured to the magnetic field at this time. Ia1/Ia2 [Ip1 and]/Ip2 is written together to Table 1.

[0018]

[Table 1]

試　料	合金組成	熱間加工方法	温度／℃	軟磁性相体積比率	I_{a1}/I_{p1}	I_{a2}/I_{p2}
実施例１	$Nd_8Fe_{78}B_{15}$	①	850	0.60	0.85	0.83
実施例２	$Nd_4Fe_{78}B_{18}$	②	750	0.85	0.88	0.88
実施例３	$Nd_9Fe_{86}B_5$	②	900	0.18	0.58	0.55
実施例４	$Nd_8Fe_{87}B_5$	②	700	0.22	0.52	0.49
実施例５	$Nd_8Fe_{77}Co_{10}B_4$	②	800	0.24	0.45	0.44
実施例６	$Nd_5Fe_{82}Co_{10}B_3$	②	750	0.50	0.35	0.34
実施例７	Sm_6Co_{94}	②	1000	0.31	0.50	0.49
実施例８	$Sm_7Fe_{13}Co_{80}$	②	1000	0.25	0.55	0.56
実施例９	$Sm_4Fe_{92}Ti_4$	②	900	0.42	0.51	0.49
実施例１０	$Sm_5Fe_{80}Co_{10}Ti_5$	②	900	0.30	0.76	0.76
実施例１１	$Sm_5Fe_{85}Mo_{10}$	②	900	0.11	0.88	0.85
実施例１２	$Sm_4Fe_{87}Si_5Cu_3$	②	850	0.25	0.77	0.75
実施例１３	Sm_6Fe_{94}-N_x	③	600	0.53	0.81	0.82
実施例１４	$Sm_4Fe_{80}Co_{16}$-N_x	③	600	0.50	0.84	0.84
実施例１５	$Nd_7Zr_4Fe_{89}$-N_x	③	600	0.21	0.93	0.91
実施例１６	$Nd_5Zr_3Fe_{87}Co_5$-N_x	③	600	0.29	0.88	0.86
比較例１	$Nd_9Fe_{85}B_6$	加熱のみ	850	0.18	—	0.98

[0019] (Example 1 of a comparison) After using as powder the quenching thin band alloy produced like the example by the presentation shown in Table 1, it is among Ar ambient atmosphere as it is. It heated, asked and came out at 850 degrees C, and compression processing was not

performed at all. When this was hardened from paraffin all over 14kOe magnetic field as it was and the ratios Ia2/Ip2 of Ip2 and Ia2 were measured similarly, it is 0.98 and the magnetic anisotropy was not accepted.

[0020]

[Effect of the Invention] According to this invention, the anisotropy rare earth permanent magnet and magnet powder to which the easy axis was equal can be obtained.

[Translation done.]

(19)日本国特許庁（ＪＰ）　(12) **公開特許公報**（Ａ）　(11)特許出願公開番号

特開平11－97222

(43)公開日　平成11年(1999)４月９日

(51)Int.Cl.⁶	識別記号	ＦＩ		
Ｈ０１Ｆ　1/053		Ｈ０１Ｆ　1/04		Ｈ
Ｂ２２Ｆ　1/00		Ｂ２２Ｆ　1/00		Ｙ
Ｈ０１Ｆ　1/06		Ｈ０１Ｆ　7/02		Ｃ
7/02		Ｃ２２Ｃ　38/00	３０３	Ｄ
// Ｃ２２Ｃ　38/00	３０３	Ｈ０１Ｆ　1/06		Ａ

審査請求　未請求　請求項の数14　ＯＬ　（全　６　頁）

(21)出願番号　特願平9－255255

(22)出願日　平成９年(1997)９月19日

(71)出願人　000002060
信越化学工業株式会社
東京都千代田区大手町二丁目６番１号

(72)発明者　野村　忠雄
福井県武生市北府２丁目１番５号　信越化学工業株式会社磁性材料研究所内

(72)発明者　大橋　健
福井県武生市北府２丁目１番５号　信越化学工業株式会社磁性材料研究所内

(74)代理人　弁理士　山本　亮一　（外１名）

(54)【発明の名称】　異方性希土類永久磁石材料及び磁石粉末

(57)【要約】　（修正有）

【課題】　硬磁性相と軟磁性相が微細分散し、かつ硬磁性相の磁化容易軸が揃っている組織を有した異方性希土類永久磁石材料及び磁石粉末を得る。

【解決手段】　硬磁性相と軟磁性相が微細に分散した内部組織を有する希土類永久磁石において、急冷薄帯の合金原料が加熱された状態で一軸方向に加圧変形されることによって、硬磁性相の磁化容易軸が一方向に揃えられたことを特徴とする異方性希土類永久磁石、また当該磁石を粉砕してなる異方性希土類磁石粉末。

【特許請求の範囲】

【請求項１】　硬磁性相と軟磁性相が微細に分散した内部組織を有する希土類永久磁石において、急冷薄帯の合金原料が加熱された状態で一軸方向に加圧変形されることによって、硬磁性相の磁化容易軸が一方向に揃えられたことを特徴とする異方性希土類永久磁石。

【請求項２】　硬磁性相が$Nd_2Fe_{14}B$であり、軟磁性相がbcc-Fe、Fe_3B、Fe_2Bのうち少なくとも１種以上を含んでおり、かつ軟磁性相の体積割合が10～90％である請求項１記載の異方性希土類永久磁石。

【請求項３】　硬磁性相が$Nd_2(Fe,Co)_{14}B$ であり、軟磁性相がFe-Co 合金、$(Fe,Co)_3B$ 、$(Fe,Co)_2B$ のうち少なくとも１種以上を含んでおり、かつ軟磁性相の体積割合が10～90％である請求項１記載の異方性希土類永久磁石。

【請求項４】　硬磁性相がSm_2Co_{17} もしくは$Sm_2(Fe,Co)_{17}$であり、軟磁性相がCoもしくは Fe-Co合金を含んでおり、かつ軟磁性相の体積割合が10～90％である請求項１記載の異方性希土類永久磁石。

【請求項５】　硬磁性相が$Sm(Fe,M1)_{12}$ もしくは$Sm(Fe,Co,M1)_{12}$であり、軟磁性相がbcc-Feもしくは Fe-Co合金、Fe-M1 合金、Fe-M1 金属間化合物、Fe-Co-M1合金、Fe-Co-M1金属間化合物のうち少なくとも１種以上を含んでおり（ただしM1は、Ti、Ｖ、Cr、Mo、Si、Cuのうちの１種以上）、かつ軟磁性相の体積割合が10～90％である請求項１記載の異方性希土類永久磁石。

【請求項６】　硬磁性相がSm_2Fe_{17} 窒化物もしくは$Sm_2(Fe,Co)_{17}$窒化物であり、軟磁性相がbcc-Feもしくは Fe-Co合金を含んでおり、かつ軟磁性相の体積割合が10～90％である請求項１記載の異方性希土類永久磁石。

【請求項７】　硬磁性相が$(Nd,M2)Fe_X$窒化物もしくは$(Nd,M2)(Fe,Co)_X$ 窒化物（ただし５≦Ｘ≦12）であり、軟磁性相がbcc-Fe、Fe-M2 合金、Fe-M2 金属間化合物、Fe-Co 合金、Fe-Co-M2合金、Fe-Co-M2金属間化合物のうち少なくとも１種以上を含んでおり（ただしM2は、Ti、Ｖ、Zr、Nb、Hf、Ta、Si、Alのうちの１種以上）、かつ軟磁性相の体積割合が10～90％である請求項１記載の異方性希土類永久磁石。

【請求項８】　請求項１記載の磁石を粉砕することにより得られる異方性希土類磁石粉末。

【請求項９】　硬磁性相が$Nd_2Fe_{14}B$であり、軟磁性相がbcc-Fe、Fe_3B、Fe_2Bのうち少なくとも１種以上を含んでおり、かつ軟磁性相の体積割合が10～90％である請求項８記載の異方性希土類永久磁石粉末。

【請求項１０】　硬磁性相が$Nd_2(Fe,Co)_{14}B$ であり、軟磁性相がFe-Co 合金、$(Fe,Co)_3B$ 、$(Fe,Co)_2B$ のうち少なくとも１種以上を含んでおり、かつ軟磁性相の体積割合が10～90％である請求項８記載の異方性希土類永久磁石粉末。

【請求項１１】　硬磁性相がSm_2Co_{17} もしくは$Sm_2(Fe,Co)_{17}$であり、軟磁性相がCoもしくは Fe-Co合金を含んでおり、かつ軟磁性相の体積割合が10～90％である請求項８記載の異方性希土類永久磁石粉末。

【請求項１２】　硬磁性相が$Sm(Fe,M1)_{12}$ もしくは$Sm(Fe,Co,M1)_{12}$であり、軟磁性相がbcc-Feもしくは Fe-Co合金、Fe-M1 合金、Fe-M1 金属間化合物、Fe-Co-M1合金、Fe-Co-M1金属間化合物のうち少なくとも１種以上を含んでおり（ただしM1は、Ti、Ｖ、Cr、Mo、Si、Cuのうちの１種以上）、かつ軟磁性相の体積割合が10～90％である請求項８記載の異方性希土類永久磁石粉末。

【請求項１３】　硬磁性相がSm_2Fe_{17} 窒化物もしくは$Sm_2(Fe,Co)_{17}$窒化物であり、軟磁性相がbcc-Feもしくは Fe-Co合金を含んでおり、かつ軟磁性相の体積割合が10～90％である請求項８記載の異方性希土類永久磁石粉末。

【請求項１４】　硬磁性相が$(Nd,M2)Fe_X$窒化物もしくは$(Nd,M2)(Fe,Co)_X$ 窒化物（ただし５≦Ｘ≦12）であり、軟磁性相がbcc-Fe、Fe-M2 合金、Fe-M2 金属間化合物、Fe-Co 合金、Fe-Co-M2合金、Fe-Co-M2金属間化合物のうち少なくとも１種以上を含んでおり（ただしM2は、Ti、Ｖ、Zr、Nb、Hf、Ta、Si、Alのうちの１種以上）、かつ軟磁性相の体積割合が10～90％である請求項８記載の異方性希土類永久磁石粉末。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、異方性希土類永久磁石及び磁石粉末に関する。

【０００２】

【従来の技術】現在、希土類永久磁石は Sm-Co系、Nd-Fe-B 系などが量産化されているが、特に Nd-Fe-B磁石は高い磁気特性を有し、またSm-Co 系磁石に比較して材料コストが低いことから需要が増大している。このNd-Fe-B 永久磁石には、いくつかの製法が開発されている。もっとも工業化の進んでいる製造方法は焼結法である。この焼結磁石は、硬磁気特性を有する$Nd_2Fe_{14}B$を主相とし、さらにNdリッチ相、$Nd_{1.1}Fe_4B_4$相（Ｂリッチ相）を含んだ組織を有するが、製法としては$Nd_2Fe_{14}B$化学量論組成よりも若干Nd、Ｂ過剰な組成で溶解した合金を数μmの微粉に粉砕し磁場中成形により磁化容易軸を一方向に揃えた後、1100℃付近の温度で焼結し、さらに低温時効処理する（M.Sagawa et al,Japanese Journal of Applied Physics 26(1987) 785 ）方法が知られており、$Nd_2Fe_{14}B$主相が周囲を取り囲んだNdリッチ相により界面をクリーニングされることで保磁力が発現し、異方性永久磁石となる。他方、磁石組成の溶湯を回転ロール上に吹き出して高速凝固させるメルトスパン法によって急冷薄帯合金を作製し、これをもとに磁石を作製する方法も開発されている（R.W.Lee,Physics Letter 46(1985)790など）。この磁石は同じく$Nd_2Fe_{14}B$を主相とするものの、結晶粒径が20～ 100nmと焼結磁石に比べて小さく、単磁区粒径であることが保磁力の起因となっている。これに

は三つのタイプがある。第１のタイプは急冷薄帯を粉砕したものを樹脂と混合、成形してボンド磁石とするもので、これは工程が簡単であるものの、磁化容易軸が一方向に揃わず等方性で、かつ充填密度が低いために、磁気特性は劣る。第２のタイプは、該急冷薄帯粉をホットプレスして等方性バルク磁石とするものであり、第３のタイプはこれにさらに熱間加工を施し加圧方向に磁化容易軸を揃えるものである（特開昭６０－１００４０２号公報など）。

【０００３】一方、さらなる高性能の次世代磁石探索が行われている中で、近年ナノコンポジット磁石が注目を集めている（E.F.Kneller et al,IEEE Transaction Magnetics 27(1991)3588 他）。上記の焼結磁石、急冷磁石は硬磁性相である$Nd_2Fe_{14}B$相を主相としているものの、bcc-FeやFe_3B、Fe_2BなどのFeリッチな軟磁性相は含んでいない。これに対し、ナノコンポジット磁石は硬磁性相と軟磁性相が数十nmオーダーで微細分散した組織からなり、両相の磁化が交換相互作用で結び付くことによって軟磁性相の磁化は容易に反転せず、全体として単一な硬磁性相のように振る舞うものである。既存材料の組み合わせでも、これによって保磁力を損なうことなく、より高い飽和磁化を得られる可能性がある。計算では異方性化した $Sm_2Fe_{17}N_3$／Fe-Co において、$(BH)_{max}$ ＝137 MGOeの値が報告されている（R.Skomski et al,Physical Review B 48(1993) 15812）。ナノコンポジット磁石を実際に作製した実験例としては、これまで$Nd_2Fe_{14}B$／Fe_3B（R.Coehoorn et al,Journal de Physique 49(1988)C8-669 ）、$Nd_2Fe_{14}B$／Fe（特開平７－１７３５０１号公報、特開平７－１７６４１７号公報や、L.Withanawasam et al,Journal of Applied Physics 76(1994)7065など）や $Sm_2Fe_{17}N_3$／Fe（J.Ding et al,Journal of Magnetism and Magnetic Materials 124(1993)L1）などの組み合わせが報告されている。しかし、これらの研究で行われている微細分散組織の作製方法としては、いずれもメルトスパン法による急冷薄帯やメカニカルアロイング（MA）法により得られたアモルファス合金粉末を熱処理して微結晶化する手段が取られているため、このままでは前述の第１タイプと同じく結晶方位が揃えることができず、磁気的に等方性のものしか得られない。したがって現時点まで異方性ナノコンポジット磁石を作製した報告はなく、その実現が待たれている。

【０００４】

【発明が解決しようとする課題】このように磁気異方性を有するナノコンポジット永久磁石は、計算や理論では報告されているものの、これまで実際に作製された報告はない。本発明は、従来の作製方法にさらなる改良を加えることにより、硬磁性相と軟磁性相が微細に分散し、かつ硬磁性相の磁化容易軸が揃っている組織を有した異方性希土類永久磁石を実現させることを課題とする。

【０００５】

【課題を解決するための手段】本発明者らはかかる問題を解決するために鋭意検討した結果、熱処理により硬磁性相と軟磁性相が微細分散析出するような組成の急冷薄帯合金を熱間加工することにより、上記希土類永久磁石が得られることを見出し、諸条件を確立して本発明を完成させた。その要旨は、硬磁性相と軟磁性相が微細に分散した内部組織を有する希土類永久磁石において、急冷薄帯の合金原料が加熱された状態で一軸方向に加圧変形されることによって、硬磁性相の磁化容易軸が一方向に揃えられた異方性希土類永久磁石及びこの粉砕により得られる異方性希土類磁石粉末にある。

【０００６】

【発明の実施の形態】上記異方性希土類永久磁石の硬磁性相は$Nd_2Fe_{14}B$、$Nd_2(Fe,Co)_{14}B$ 、Sm_2Co_{17}、$Sm_2(Fe,Co)_{17}$、$Sm(Fe,M1)_{12}$ 、$Sm(Fe,Co,M1)_{12}$（ただしM1はTi、Ｖ、Cr、Mo、Si、Cuのうちの１種以上）、Sm_2Fe_{17} 窒化物、$Sm_2(Fe,Co)_{17}$窒化物、$(Nd,M2)Fe_X$窒化物もしくは$(Nd,M2)(Fe,Co)_X$ 窒化物（ただし５≦Ｘ≦12、M2はTi、Ｖ、Zr、Nb、Hf、Ta、Si、Alのうちの１種以上）などから選ばれる相であり、軟磁性相はbcc-Fe、Fe_3B、Fe_2B、Fe-Co 合金、$(Fe,Co)_3B$ 、$(Fe,Co)_2B$ 、Fe-M1 合金、Fe-M1 金属間化合物、Fe-Co-M1合金、Fe-Co-M1金属間化合物、Fe-M2 合金、Fe-M2 金属間化合物、Fe-Co-M2合金、Fe-Co-M2金属間化合物などの少なくとも１種以上を含んでおり、かつ軟磁性相の体積割合が10～90％である。

【０００７】また、上記磁石粉末の硬磁性相は$Nd_2Fe_{14}B$、$Nd_2(Fe,Co)_{14}B$ 、Sm_2Co_{17} 、$Sm_2(Fe,Co)_{17}$、$Sm(Fe,M1)_{12}$ 、$Sm(Fe,Co,M1)_{12}$（ただしM1はTi、Ｖ、Cr、Mo、Si、Cuのうちの１種以上）、Sm_2Fe_{17} 窒化物、$Sm_2(Fe,Co)_{17}$窒化物、$(Nd,M2)Fe_X$窒化物もしくは$(Nd,M2)(Fe,Co)_X$ 窒化物（ただし５≦Ｘ≦12、M2はTi、Ｖ、Zr、Nb、Hf、Ta、Si、Alのうちの１種以上）などから選ばれる相であり、軟磁性相はbcc-Fe、Fe_3B、Fe_2B、Fe-Co 合金、$(Fe,Co)_3B$ 、$(Fe,Co)_2B$ 、Fe-M1 合金、Fe-M1 金属間化合物、Fe-Co-M1合金、Fe-Co-M1金属間化合物、Fe-M2 合金、Fe-M2 金属間化合物、Fe-Co-M2合金、Fe-Co-M2金属間化合物などの少なくとも１種以上を含んでおり、かつ軟磁性相の体積割合が10～90％である。

【０００８】以下に、本発明を詳述に説明する。本発明において、その最終的な組織は、硬磁性相と軟磁性相が微細に分散しかつ硬磁性相の磁化容易軸が一方向に揃えられた状態からなっている。硬磁性相は$Nd_2Fe_{14}B$、$Nd_2(Fe,Co)_{14}B$ 、Sm_2Co_{17} 、$Sm_2(Fe,Co)_{17}$、$Sm(Fe,M1)_{12}$ 、$Sm(Fe,Co,M1)_{12}$（ただしM1はTi、Ｖ、Cr、Mo、Si、Cuのうちの１種以上、以下同）、Sm_2Fe_{17} 窒化物、$Sm_2(Fe,Co)_{17}$窒化物、$(Nd,M2)Fe_X$窒化物もしくは$(Nd,M2)(Fe,Co)_X$窒化物（ただし５≦Ｘ≦12、M2はTi、Ｖ、Zr、Nb、Hf、Ta、Si、Alのうちの１種以上、以下同）などから選ばれる相であり、軟磁性相はbcc-Fe、Fe_3B、Fe_2B、Fe-Co 合金、$(Fe,Co)_3B$ 、$(Fe,Co)_2B$ 、Fe-M1 合金、Fe

-M1 金属間化合物、Fe-Co-M1合金、Fe-Co-M1金属間化合物、Fe-M2 合金、Fe-M2 金属間化合物、Fe-Co-M2合金、Fe-Co-M2金属間化合物などの少なくとも１種以上を含んでおり、かつ軟磁性相の体積割合が10～90%である。

【０００９】この磁石の作製は以下のように行なわれる。まず所定組成合金の溶融体を急冷してアモルファスもしくはアモルファスと微結晶の混在した急冷薄帯合金を作製する。このときの組成は、熱処理を施すことにより硬磁性相と軟磁性相が微細分散析出するような組成とする。また最終的な試料における軟磁性相の体積割合は10～90%となるようにする。10%未満では飽和磁化の向上がわずかであり、ナノコンポジット磁石とするメリットがない。また90%を超えると硬磁性相割合が少なすぎて、磁石の保磁力低下が著しい。

【００１０】以下、具体的な材料について記述すると、例えば硬磁性相／軟磁性相の組み合わせが$Nd_2Fe_{14}B$／bcc-Feの場合には Fe-２～10at% Nd-１～８at%Ｂ程度の組成とするのが好ましく、$Nd_2Fe_{14}B$／Fe_3Bの場合には Fe-２～10at% Nd-15～25at%Ｂ程度の組成が好ましい。また$Nd_2Fe_{14}B$／Fe_2Bの場合には Fe-２～10at% Nd-25～35at%Ｂ程度の組成が好ましい。またこれらの中間組成を選ぶことにより、bcc-Fe、Fe_3B、Fe_2Bなどの軟磁性相が共存する組織にすることもできる。

【００１１】Feの一部をCoで置換することにより、$Nd_2(Fe,Co)_{14}B$ ／Fe-Co 合金、$Nd_2(Fe,Co)_{14}B$ ／$(Fe,Co)_3B$ 、$Nd_2(Fe,Co)_{14}B$ ／$(Fe,Co)_2B$ などの組み合わせとしてもよい。さらに特性を向上させるために、Al、Si、Ti、Ｖ、Cr、Mn、Ni、Cu、Zn、Ga、Ge、Zr、Nb、Mo、Tc、Ru、Rh、Pd、Ag、Cd、In、Sn、Hf、Ta、Ｗ、Re、Os、Ir、Pt、Au、Tl、Pb、Biなどから選ばれる元素をFeを置換する形で何種類か添加してもよい。このとき添加量が多すぎると飽和磁化の低下を招くため、置換量は多くとも５at%以下が望ましい。また保磁力をさらに向上させるためにNdの一部をPr、Tb、Dy、Hoなど他の希土類元素で置換してもよい。

【００１２】硬磁性相／軟磁性相がSm_2Co_{17} ／Coのときは、 Co-２～10at%Sm程度の組成が好ましい。またCoの一部をFeで置換して$Sm_2(Fe,Co)_{17}$／Fe－Co合金としたり、特性向上のために上述の元素群で置換したりしてもよいし、さらにSmの一部をCeなど他の希土類元素やミッシュメタルで置換してもよい。

【００１３】硬磁性相／軟磁性相が $Sm(Fe,M1)_{12}$／bcc-Feの場合、M1元素は上記1-12結晶構造を安定化するために必要であるが、元素によって最適な組成が異なる。例えば、M1＝Tiのときは$SmFe_{11}Ti$が安定であるし、Ｖ、Cr、Mo、Siなどのときは$SmFe_{10}M1_2$ が安定化しやすいので、元素に合わせて出発組成を調整する。また軟磁性相はbcc-Fe以外にFe-M1 合金、Fe-M1 金属間化合物であってもよい。さらにFeの一部をCoで置換して$Sm(Fe,Co,M1)_{12}$／Fe-Co 合金や、$Sm(Fe,Co,M1)_{12}$／Fe-Co-M1合金、$Sm(Fe,Co,M1)_{12}$／Fe-Co-M1金属間化合物としたり、さらに特性を向上させるためにAl、Mn、Ni、Cu、Zn、Ga、Ge、Zr、Nb、Tc、Ru、Rh、Pd、Ag、Cd、In、Sn、Hf、Ta、Ｗ、Re、Os、Ir、Pt、Au、Tl、Pb、Biなどから選ばれる元素をFeを置換する形で何種類か添加してもよい。さらにSmの一部を他の希土類元素で置換してもよい。

【００１４】硬磁性相／軟磁性相がSm_2Fe_{17}窒化物／bcc-Feのときは、 Fe-２～10at%Sm程度の組成が好ましい。硬磁性相の窒化は後工程の熱処理時に同時に行う。この場合もまた、Feの一部をCoで置換して$Sm_2(Fe,Co)_{17}$窒化物／Fe-Co 合金としたり、上述の元素群で置換したりしてもよいし、Smの一部を他の希土類元素で置換してもよい。

【００１５】硬磁性相が$(Nd,M2)Fe_X$窒化物もしくは$(Nd,M2)(Fe,Co)_X$ 窒化物の場合、この窒化物相の基となる$(Nd,M2)Fe_X$化合物については$NdFe_2$ 、Nd_2Fe_{17} など２元系安定相と同じ結晶構造を有するものの他、1-7 相、1-12相のように多元系で安定化する化合物や準安定相など多くの化合物が存在し、したがってその窒化物も数多くあるが、Ｘが５よりも小さい場合は化合物が室温で強磁性となりがたく、Ｘが12よりも大きいときは十分な磁気異方性を有しにくい。ゆえに硬磁性相である$(Nd,M2)Fe_X$窒化物のＸは５≦Ｘ≦12の範囲が望ましい。また軟磁性相もbcc-Feに限定されず、Fe-M2 合金や、Fe-M2 金属間化合物、あるいはこれらが共存するものであってよい。この場合もまた、硬磁性相の窒化は後工程の熱処理時に同時に行うものであり、さらにFeの一部をCoで置換して$(Nd,M2)(Fe,Co)_X$ 窒化物／Fe-Co 合金や$(Nd,M2)(Fe,Co)_X$窒化物／Fe-Co-M2合金、$(Nd,M2)(Fe,Co)_X$ 窒化物／Fe-Co-M2金属間化合物などとしたり、また上述の元素群で置換したりしてもよいし、Ndの一部を他の希土類元素で置換してもよい。具体的な例をいくつか挙げれば、$(Nd,Zr)Fe_7$窒化物／bcc-Fe、$(Nd,Zr)Fe_7$窒化物／Fe-Zr 、$(Nd,Zr)Fe_7$窒化物／Fe_3Zr 、$(Nd,Zr)(Fe,Co)_7$ 窒化物／Fe-Co 、$(Nd,Zr)Fe_9$窒化物／bcc-Fe、$(Nd,Zr)(Fe,Co)_9$ 窒化物／Fe-Co 、$(Nd,Zr)Fe_{10}$ 窒化物／bcc-Fe、$(Nd,Zr)(Fe,Co)_{10}$窒化物／Fe-Co 、$(Nd,Zr)Fe_{12}$ 窒化物／bcc-Fe、$(Nd,Zr)(Fe,Co)_{12}$窒化物／Fe-Co 、$(Nd,Nb)Fe_7$窒化物／bcc-Fe、$(Nd,Nb)(Fe,Co)_7$ 窒化物／Fe-Co 、$(Nd,Nb)Fe_{12}$ 窒化物／bcc-Fe、$(Nd,Nb)(Fe,Co)_{12}$窒化物／Fe-Co 、$(Nd,Hf)Fe_7$窒化物／bcc-Fe、$(Nd,Hf)(Fe,Co)_7$ 窒化物／Fe-Co 、$(Nd,Hf)Fe_{12}$ 窒化物／bcc-Fe、$(Nd,Hf)(Fe,Co)_{12}$窒化物／Fe-Co などがあるがこれらに限定されるものではない。

【００１６】急冷方法として回転ロール法、スプラット法、ガスアトマイズ法などが知られているが、なかでも回転ロール法による急冷薄帯は簡便でかつ品質の良いものが得られる。Cu製ロールの場合10m/s 以上、50m/s 以下のロール速度で良好な特性が得られる。10m/s 未満ではアモルファスの試料を得ることができず、50m/s を超

えると後の熱処理工程での結晶化が困難になる。次にこの試料を粉砕してから高温で加圧変形する。加圧変形の方法としてホットプレスによる固化成形後にホットフォームを行う方法（特開昭６０－１００４０２号公報参照）、押出加工法（小嶋ら、日本応用磁気学会誌12,(1988)219）、パック圧延法（坂本ら、日本応用磁気学会誌16,(1992)147）、衝撃圧を利用した方法（特公平７－８７１５６号公報参照）などが用いられる。これらはいずれも従来より Nd-Fe-B系異方性磁石の作製方法として用いられてきたものであるが、$Nd_2Fe_{14}B$化学量論組成よりもNdリッチな組成について試みられているのに対し、本発明はいずれも硬磁性相の化学量論組成よりも希土類の少ない組成であり、bcc-Fe、Fe-Co 合金その他の軟磁性相を10～90％含んでおり、かつ硬磁性相と磁気的に交換結合しているような組成を対象とするものである。このようにして得られたバルク試料は、硬磁性相と軟磁性相とが微細に分散し、かつ硬磁性相の磁化容易軸が一方向に揃った組織からなる異方性希土類永久磁石となる。さらにこのバルク磁石を粉砕することにより、異方性を有するナノコンポジット希土類磁石粉末が得られる。これを樹脂と混合成形すれば高特性のボンド磁石を作製することができる。

【００１７】

【実施例】次に、本発明について実施例を挙げて具体的に説明するが、本発明はこれらに限定されるものではない。

（実施例１～１６）各純金属を表１に示す所定組成となるように秤量した後、アーク溶解で合金を得た。これを石英ノズル内に入れてAr雰囲気中で高周波溶解し、45m/s の周速度で回転しているCu製ロール上に射出して急冷薄帯を作製した。この急冷薄帯を粉砕して粉末としたものを以下のいずれかで熱間加工した。なお③ の方法は硬磁性相を窒化物とするときに行った。

①　Ar雰囲気中ホットプレスで固化後、再びAr雰囲気中でホットフォーム。

②　Cu製容器に充填し、Ar雰囲気中で加熱した後、プレス圧縮。

③　Cu製容器に充填し、N_2 雰囲気中で加熱して窒化物を形成後、プレス圧縮。

表１に、選択した方法の番号及びその時の熱処理温度を併記する。作製後試料の内部組織を TEMもしくは SEM反射電子像で観察し、各々試料において該当する軟磁性相の存在を確認するとともに、その体積比率を判定した。磁気異方性の判定は、立方形に切り出した試料に20ｋOe磁場印加したときの圧縮方向の磁化の大きさI_{p1}と、圧縮に垂直な方向での磁化の大きさI_{a1}の比I_{a1}/I_{p1}により行った。I_{a1}/I_{p1}の値が小さいほど磁気異方性が大きいことを表わす。また同バルク試料をボールミル粉砕した粉末を14ｋOe磁場中にてパラフィンで固め、このときの磁場に対して平行方向及び垂直方向に20ｋOe磁場印加したときの磁化の大きさI_{p2}、I_{a2}の比I_{a2}/I_{p2}を測定した。I_{a1}/I_{p1}、I_{a2}/I_{p2}を表１に併記する。

【００１８】

【表１】

試　料	合金組成	熱間加工方法	温度／℃	軟磁性相体積比率	I_{a1}/I_{p1}	I_{a2}/I_{p2}
実施例１	$Nd_6Fe_{78}B_{16}$	①	850	0.60	0.65	0.83
実施例２	$Nd_4Fe_{78}B_{18}$	②	750	0.85	0.88	0.88
実施例３	$Nd_9Fe_{86}B_5$	②	900	0.18	0.58	0.55
実施例４	$Nd_8Fe_{87}B_5$	②	700	0.22	0.52	0.49
実施例５	$Nd_9Fe_{77}Co_{10}B_4$	②	800	0.24	0.45	0.44
実施例６	$Nd_5Fe_{82}Co_{10}B_3$	②	750	0.50	0.35	0.34
実施例７	Sm_6Co_{94}	②	1000	0.31	0.50	0.49
実施例８	$Sm_7Fe_{13}Co_{80}$	②	1000	0.25	0.55	0.56
実施例９	$Sm_4Fe_{92}Ti_4$	②	900	0.42	0.51	0.49
実施例１０	$Sm_5Fe_{80}Co_{10}Ti_5$	②	900	0.30	0.76	0.76
実施例１１	$Sm_5Fe_{85}Mo_{10}$	②	900	0.11	0.88	0.85
実施例１２	$Sm_4Fe_{87}Si_6Cu_3$	②	850	0.25	0.77	0.75
実施例１３	Sm_6Fe_{94}-N_X	③	600	0.53	0.81	0.82
実施例１４	$Sm_4Fe_{80}Co_{16}$-N_X	③	600	0.50	0.84	0.84
実施例１５	$Nd_7Zr_4Fe_{89}$-N_X	③	600	0.21	0.93	0.91
実施例１６	$Nd_5Zr_3Fe_{87}Co_5$ N_X	③	600	0.29	0.88	0.86
比較例１	$Nd_9Fe_{85}B_6$	加熱のみ	850	0.18	―	0.98

【００１９】（比較例１）表１に示す組成で実施例と同様に作製した急冷薄帯合金を粉末とした後、そのままAr

雰囲気中 850℃で加熱したのみで何ら圧縮加工を行わなかった。これをそのまま14ｋOe磁場中にてパラフィンで固め、同様にI_{p2}、I_{a2}の比I_{a2}／I_{p2}を測定したところ、0.98であり、磁気異方性は認められなかった。

【００２０】

【発明の効果】本発明によれば、磁化容易軸が揃った異方性希土類永久磁石と磁石粉末を得ることができる。